



Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography¹

This standard is issued under the fixed designation D4815; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers the determination of ethers and alcohols in gasolines by gas chromatography. Specific compounds determined are methyl *tert*-butylether (MTBE), ethyl *tert*-butylether (ETBE), *tert*-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, *n*-propanol, isobutanol, *tert*-butanol, *sec*-butanol, *n*-butanol, and *tert*-pentanol (*tert*-amylalcohol).

1.2 Individual ethers are determined from 0.20 to 20.0 mass %. Individual alcohols are determined from 0.20 to 12.0 mass %. Equations used to convert to mass % oxygen and to volume % of individual compounds are provided. At concentrations <0.20 mass %, it is possible that hydrocarbons may interfere with several ethers and alcohols. The reporting limit of 0.20 mass % was tested for gasolines containing a maximum of 10 volume % olefins. It may be possible that for gasolines containing >10 volume % olefins, the interference may be >0.20 mass %. **Annex A1** gives a chromatogram showing the interference observed with a gasoline containing 10 volume % olefins.

1.3 Alcohol-based fuels, such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol, are specifically excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.4 Benzene, while detected, cannot be quantified using this test method and must be analyzed by alternate methodology (see Test Method **D3606**).

1.5 The values stated in SI units are to be regarded as standard. Alternate units, in common usage, are also provided to increase clarity and aid the users of this test method.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards*:²

D1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent³

D3606 Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4420 Test Method for Determination of Aromatics in Finished Gasoline by Gas Chromatography³

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *low volume connector*—a special union for connecting two lengths of tubing 1.6-mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.1.2 *oxygenate*—any oxygen-containing organic compound that can be used as a fuel or fuel supplement, for example, various alcohols and ethers.

3.1.3 *split ratio*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by

$$\text{split ratio} = (S + C)/C \quad (1)$$

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee **D02.04.0L** on Gas Chromatography Methods.

Current edition approved Oct. 1, 2009. Published November 2009. Originally approved in 1989. Last previous edition approved in 2004 as D4815-04. DOI: 10.1520/D4815-09.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

*A Summary of Changes section appears at the end of this standard.

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.1.4 *tert*-amyl alcohol—*tert*-pentanol.

3.2 *Acronyms*:

3.2.1 *DIPE*—diisopropylether.

3.2.2 *ETBE*—ethyl *tert*-butylether.

3.2.3 *MTBE*—methyl *tert*-butylether.

3.2.4 *TAME*—*tert*-amyl methylether.

3.2.5 *TCEP*—1,2,3-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

3.2.6 *WCOT*—a type of capillary gas chromatographic column prepared by coating the inside of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 An appropriate internal standard, such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether), is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column, which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

4.2 After methylcyclopentane, but before DIPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a WCOT nonpolar column. The alcohols and ethers elute from the nonpolar column in boiling point order, before elution of any major hydrocarbon constituents.

4.3 After benzene and TAME elute from the nonpolar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons.

4.4 The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and Use

5.1 Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust, and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

6. Apparatus

6.1 *Chromatograph*—While any gas chromatographic system, which is capable of adequately resolving the individual ethers and alcohols that are presented in Table 1, can be used for these analyses, a gas chromatographic instrument, which can be operated at the conditions given in Table 2 and has a column switching and backflushing system equivalent to Fig. 1, has been found acceptable. Carrier gas flow controllers shall be capable of precise control where the required flow rates are

TABLE 1 Pertinent Physical Constants and Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table 2

Component	Retention Time, Min.	Relative Retention Time		Molecular Mass	Relative Density at 15.56/15.56°C
		(MTBE = 1.00)	(DME = 1.00)		
Water	2.90	0.58	0.43	18.0	1.000
Methanol	3.15	0.63	0.46	32.0	0.7963
Ethanol	3.48	0.69	0.51	46.1	0.7939
Isopropanol	3.83	0.76	0.56	60.1	0.7899
<i>tert</i> -Butanol	4.15	0.82	0.61	74.1	0.7922
<i>n</i> -Propanol	4.56	0.90	0.67	60.1	0.8080
MTBE	5.04	1.00	0.74	88.2	0.7460
<i>sec</i> -Butanol	5.36	1.06	0.79	74.1	0.8114
DIPE	5.76	1.14	0.85	102.2	0.7282
Isobutanol	6.00	1.19	0.88	74.1	0.8058
ETBE	6.20	1.23	0.91	102.2	0.7452
<i>tert</i> -Pentanol	6.43	1.28	0.95	88.1	0.8170
1,2-Dimethoxyethane (DME)	6.80	1.35	1.00	90.1	0.8720
<i>n</i> -Butanol	7.04	1.40	1.04	74.1	0.8137
TAME	8.17	1.62	1.20	102.2	0.7758

TABLE 2 Chromatographic Operation Conditions

Temperatures	Flows, mL/min	Carrier Gas: Helium
Column Oven	60	to injector 75
Injector, °C	200	Column 5
Detector—TCD, °C	200	Auxiliary 3
—FID, °C	250	Makeup 18
Valve °C	60	
		Sample size, µL ^A 1.0–3.0
		Split ratio 15:1
		Backflush, min 0.2–0.3
		Valve reset time 8–10 min
		Total Analysis time 18–20 min

^A Sample size must be adjusted so that alcohols in the range of 0.1 to 12.0 mass % and ethers in the range of 0.1 to 20.0 mass % are eluted from the column and measured linearly at the detector. A sample size of 1.0 µL has been introduced in most cases.

low (see Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.1 *Detector*—A thermal conductivity detector or flame ionization detector can be used. The system shall have sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 volume % concentration of an oxygenate.

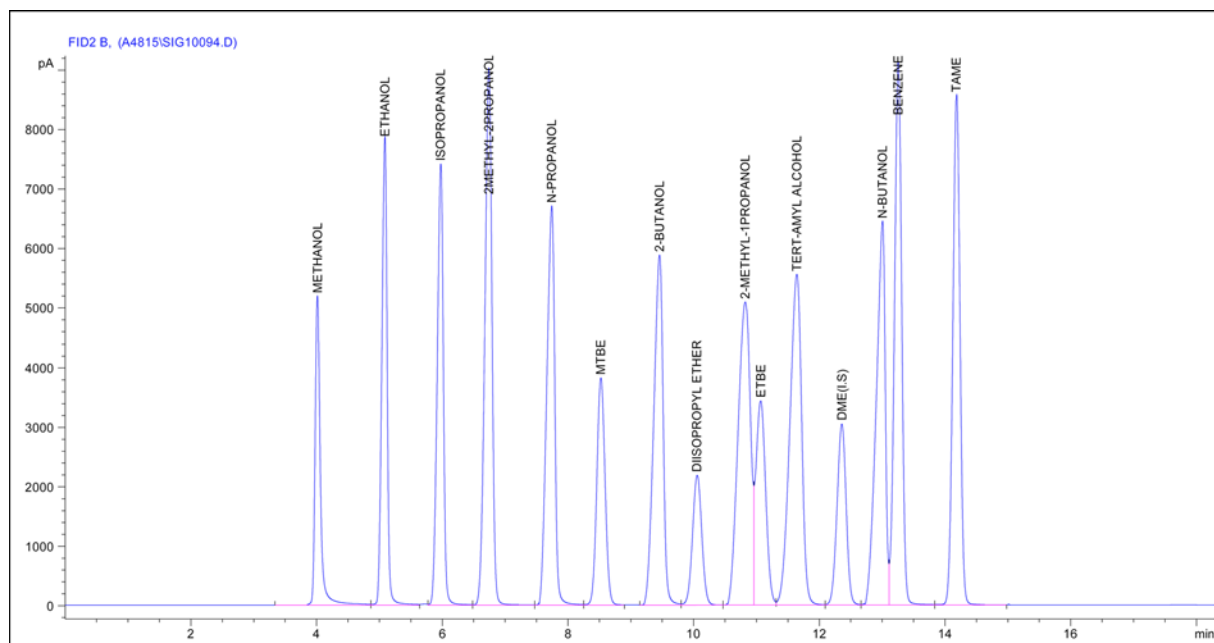
6.1.2 *Switching and Backflushing Valve*—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11 and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.1.2.1 *Valco Model No. A 4C10WP*, 1.6-mm (1/16-in.) fittings. This particular valve was used in the majority of the analyses used for the development of Section 15.

6.1.2.2 *Valco Model No. C10W*, 0.8-mm (1/32-in.) fittings. This valve is recommended for use with columns of 0.32-mm inside diameter and smaller.

6.1.2.3 Some gas chromatographs are equipped with an auxiliary oven, which can be used to contain the valve and polar column. In such a configuration, the nonpolar column is located in the main oven and the temperature can be adjusted for optimum oxygenates resolution.

6.1.3 An automatic valve switching device must be used to ensure repeatable switching times. Such a device should be synchronized with injection and data collection times.



NOTE—Detector B is optional and used to simplify setting cut times.

FIG. 1 Analysis of Oxygenates in Gasoline Schematic of Chromatographic System

6.1.4 *Injection System*—The chromatograph should be equipped with a splitting-type inlet device if capillary columns or flame ionization detection are used. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

6.1.4.1 Some gas chromatographs are equipped with on-column injectors and autosamplers, which can inject small samples sizes. Such injection systems can be used provided that sample size is within the limit of the column and detectors optimum efficiency and linearity.

6.1.4.2 Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully for introducing representative samples into the gas chromatographic inlet.

6.2 Data Presentation or Calculation, or Both:

6.2.1 *Recorder*—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less can be used to monitor detector signal. Full-scale response time should be 1 s or less with sufficient sensitivity and stability to meet the requirements of 6.1.1.

6.2.2 *Integrator or Computer*—Means shall be provided for determining the detector response. Peak heights or areas can be measured by computer, electronic integration, or manual techniques.

6.3 Columns, Two as Follows:

6.3.1 *Polar Column*—This column performs a preseparation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the nonpolar column in 6.3.2. Any column with equivalent or better chromatographic efficiency

and selectivity to that described in 6.3.1.1 can be used. The column shall perform at the same temperature as required for the column in 6.3.2, except if located in a separate auxiliary oven as in 6.1.2.3.

6.3.1.1 *TCEP Micro-Packed Column*, 560 mm (22 in.) by 1.6-mm ($\frac{1}{16}$ -in.) outside diameter by 0.76-mm (0.030-in.) inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20% (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

6.3.2 *Nonpolar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2.1 and illustrated in Fig. 2 can be used.

6.3.2.1 *WCOT Methyl Silicone Column*, 30-m (1181-in.) long by 0.53-mm (0.021-in.) inside diameter fused silica WCOT column with a 2.6- μ m film thickness of cross-linked methyl siloxane. This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

7. Reagents and Materials

7.1 *Carrier Gas*—Carrier gas appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %.

7.2 *Standards for Calibration and Identification*—Standards of all components to be analyzed and the internal standard are required for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed. (**Warning**—These materials are flammable and can be harmful or fatal if ingested or inhaled.)